

Infrared Study of Ion-Irradiated Water-Ice Mixtures with Hydrocarbons Relevant to Comets

M. H. Moore

NASA/Goddard Space Flight Center, Code 691, Greenbelt, Maryland 20771
E-mail: ummhm@lepvox.gsfc.nasa.gov

and

R. L. Hudson

Department of Chemistry, Eckerd College, St. Petersburg, Florida 33733

Received January 2, 1998; revised June 23, 1998

Ethane, methane, and acetylene were detected in Comets C/1996 B2 Hyakutake and C/1995 O1 Hale–Bopp. In order to investigate the possibility of condensed-phase synthesis of C_2H_6 in interstellar ices, we have examined the role of CH_4 and C_2H_2 in the radiation synthesis of C_2H_6 in laboratory-formed low-temperature ices. Mixtures such as $H_2O + CH_4$, $H_2O + C_2H_2$, $H_2O + CH_4 + C_2H_2$ were irradiated. Many mixtures were investigated using different concentrations of hydrocarbons. Results showed that yields of C_2H_6 from CH_4 due to dimerization, were similar to yields of C_2H_6 from C_2H_2 due to H-addition reactions. However, CH_4 was not a source of C_2H_2 , suggesting that C_2H_2 is part of the natal chemistry of these comets. Both CH_3OH and C_2H_5OH were identified in our experiments along with CO , CO_2 , HCO , H_2CO , and CH_3CHO . © 1998 Academic Press

Key Words: comet; ice, organics; infrared; irradiation.

INTRODUCTION

Abundant ethane (C_2H_6) and methane (CH_4) (Mumma *et al.* 1996), along with acetylene (C_2H_2) (Brooke *et al.* 1996), were detected in Comet C/1996 B2 Hyakutake. The abundances of C_2H_6 and CH_4 relative to H_2O were 0.4 and 0.7%, respectively, and the abundance of C_2H_2 was 0.3–0.9%. Similarly, C_2H_6 , CH_4 , and C_2H_2 were detected in Comet C/1995 O1 Hale–Bopp with preliminary production rates relative to water of C_2H_6 , 0.48%; CH_4 , 0.62%; and C_2H_2 , 0.09% (Weaver *et al.* 1998). See also Mumma *et al.* (1997) for observations giving a C_2H_6 abundance of 0.13% on an earlier date. Both comets are thought to have had previous apparitions so that observed coma molecules come from subliming interior ices and not surface ices thought to have the largest amount of radiation processing from 10^9 years in the Oort cloud region. Hyakutake and Hale–Bopp are thought to be Oort cloud objects with an

origin somewhere in the Jupiter–Neptune region. However, Mumma *et al.* (1996) point out that an abundance of C_2H_6 comparable with that of CH_4 (true for Hyakutake) implies that the ices did not originate in a thermochemically equilibrated region of the solar nebula. Instead these abundances are consistent with production of C_2H_6 in interstellar icy grain mantles which might be due to hydrogen-addition reactions to acetylene condensed from the gas phase (Charnley *et al.* 1992, 1995) or to solid-phase UV or radiation processing. Acetylene has been detected in the gas phase in interstellar regions. On the other hand, interstellar methane has been measured in both the solid and gas phase with solid-phase molecular abundances of 0.4–1.9% (Boogert *et al.* 1996) and ~4% (d’Hendecourt *et al.* 1996) relative to water.

Laboratory experiments to study the formation and distribution of organics in processed ices containing methane, ethane, and acetylene are very limited. Pure methane at 77 K has been γ -irradiated (Davis and Libby 1964) and H_2 and C_2H_6 were detected as gas-phase products. The residue was a viscous oil consisting of saturated and highly branched hydrocarbons containing an average of about 20 carbon atoms per molecule. The rate of formation of solid residues from MeV ion irradiated condensed CH_4 and their physical properties have been examined by Foti *et al.* (1984) and Calcagno *et al.* (1985). Lanzerotti *et al.* (1985) showed that solid CH_4 (20 K) decomposes under keV proton bombardment, loses H, and evolves to an ice with a C/H ratio of about 2; de Vries *et al.* (1984) detected various hydrocarbons including C_2H_2 sputtered from the surface of 15 K CH_4 during irradiation. Kaiser and Roessler (1992) compared films of CH_4 ice with closed targets of CH_4 ice irradiated with 18-MeV protons and 17-MeV $^3He^{2+}$ ions. C_2H_2 , C_2H_4 , and C_2H_6 were detected as volatile products

from both types of ice samples. Heavier hydrocarbons, cyclic compounds, and PAH molecules were detected using a variety of techniques. IR spectra of UV-photolyzed pure CH₄ (10 K) (Gerakines *et al.* 1996 and references therein) show the synthesis of C₂H₆ and C₃H₈, along with C₂H₄ and other hydrocarbons containing double and triple bonds. No evidence was found for C₂H₂; no strong evidence was found for cyclic structures. Experiments with CH₄ mixed with water are more limited. UV photolysis of the methane hydrate H₂O + CH₄ (6:1) at 77 K by Stief *et al.* (1965) produced CO, CO₂, H₂, and C₂H₆; coronal discharge experiments on a 6:1 H₂O + CH₄ ice showed darkening and the formation of a residue generally identified with alkanes, alkenes, and aldehydes (Thompson *et al.* 1987). Moore (1981) reported the IR detection of CO, CO₂, and C₂H₆ in a 1-MeV proton irradiated H₂O + CH₄ (2:5) ice at $T < 20$ K.

Experiments on radiation processing of C₂H₂ and C₂H₆ are even more limited. Radiation-induced polymerization of condensed-phase pure acetylene has been studied by Floyd *et al.* (1973 and references therein). Diacetylene, benzene, and possibly polymers of benzene were observed. During preliminary experiments using 1-MeV proton irradiation of 15 K C₂H₂ ice in our laboratory, the infrared features of diacetylene were detected along with an insoluble room temperature residue (Moore, unpublished results). Thompson *et al.* (1987) and Khare *et al.* (1993) showed that the infrared spectrum of the organic residue from a coronal-discharged H₂O + C₂H₆ ice contained alcohol, alkanes, and aldehyde or ketone features.

Because of the high abundance of C₂H₆ in Comets Hyakutake and Hale-Bopp, we were particularly interested in understanding the role of CH₄ and C₂H₂ in the formation of C₂H₆ in irradiated icy mixtures dominated by H₂O. Therefore, we discuss in this paper the results of a systematic laboratory study which is more comprehensive than any previous work. In this study, the radiation synthesis of C₂H₆ in water-dominated icy mixtures containing organics such as CH₄ and C₂H₂ was examined using IR spectroscopy. We examined several icy mixtures with different concentrations. Synthesis of C₂H₆ was observed in all experiments. The role of H addition as the formation mechanism was considered as a pathway for C₂H₆. Many other radiation products were also identified.

Current models for the origin and history of cometary ices (accretion of interstellar ices and grains or accretion from reprocessed cometary volatiles in the solar nebula or some combination thereof) suggest that it is likely that energetic processing (both ion irradiation and UV) plays an important role at some stage in affecting the composition of cometary ices. Strazzulla and Baratta (1992), for example, suggest that 10³ eV molecule⁻¹ is a possible accumulated ion dose over 10⁹ years for precometary materials. Our laboratory dose is less than 40 eV molecule⁻¹, which

is sufficient to reach a plateau in the formation rate of new species. In our experiments, protons are a source of energy for ionizations and excitations. In a H₂O-dominated mixture, major products are H atoms and hydroxyl (OH) radicals (Spinks and Wood 1990). Reactions of various organic radicals and fragments with each other, and with H and OH, result in many new products.

EXPERIMENTAL METHODS

Details concerning our laboratory setup and techniques are already in print (Moore *et al.* 1996, Hudson and Moore 1995, and references therein). Basically, H₂O-rich ice mixtures a few micrometers in thickness were formed on an aluminum mirror attached to the cooled tail ($T < 20$ K) of a cryostat in a vacuum chamber ($P \sim 10^{-8}$ torr). The mid-IR spectrum of an ice was recorded before and after irradiation with MeV protons at $T < 20$ K. Spectra were nearly always 60-scan accumulations at 4 cm⁻¹ resolution from 400 to 4000 cm⁻¹.

Gas-phase H₂O-dominated mixtures with different organics were made in a glass bulb external to the cryostat. A list of the source and purity of gases and liquids used in this experiment is given here: triply distilled H₂O with a resistance greater than 10⁷ ohm cm; CH₄, Matheson research grade, 99.999%; C₂H₂, Matheson, purified using a slush bath at 173 K; C₂H₄, Matheson research grade, 99.99%; C₂H₆, Air Products CP grade; C₃H₈, Scientific Gas Products research grade, 99.99%; CH₃OH, Sigma-Aldrich HPLC grade, 99.9%; C₂H₅OH, Pharmco, absolute; CO, Matheson research grade, 99.99%; CH₃CHO, Aldrich, 99.0%; H₂CO, Fisher, purified trioxymethylene. Gases were mixed in a glass bulb in which the concentration of each was determined by its pressure.

Ice thickness was determined by measuring laser interference fringes during deposition. Deposition rates typically were 1–5 μm h⁻¹. The ice thickness, mixture ratio (used to determine the average molecular weight), and integrated area of selected IR absorption bands were used to calculate integrated absorbances (A , in units of cm molecule⁻¹). Each A value was calculated for the most intense band unobscured by H₂O absorptions, since our objective was to measure product yields for organics in a water mixture. Table I is a summary of the A values we determined along with several values previously reported in the literature. Integrated absorbances were used to calculate the column density of molecules synthesized in an irradiated mixture (calculated by dividing the integrated area of the molecular band by the appropriate value of A). Overlapping bands were separated by standard curve fitting techniques. We assumed an ice density of 1 g cm⁻³ for all mixtures. More details about these types of calculations are given, for example, in Hudgins *et al.* (1993).

Protons from a Van de Graaff accelerator were used to

TABLE I
Summary of Spectral Values for Organic Molecules in Amorphous Water Ice

Molecule	Average ratio (H ₂ O:molecule)	Molecular density ×10 ²² (molecule cm ⁻³)	Integrated absorbance (A) (cm molecule ⁻¹)	Average band position (cm ⁻¹)	Wavelength (μm)
CH ₄	15:1	3.76	6.63 × 10 ⁻¹⁸	1302	7.69
C ₂ H ₂	15:2	2.32	3.19 × 10 ⁻¹⁸	1955	5.12
C ₂ H ₄	15:0.9	2.15	2.93 × 10 ⁻¹⁸	1436	6.96
C ₂ H ₆	15:0.8	2.01	4.16 × 10 ⁻¹⁸	1464	6.83
	15:6		4.39 × 10 ⁻¹⁸	2882	3.47
	15:6		1.05 × 10 ⁻¹⁷	2976	3.36
C ₃ H ₈	15:0.7	1.37	1.58 × 10 ⁻¹⁷	2962	3.38
CH ₃ OH	15:1.5	1.88	1.5 × 10 ⁻¹⁷ ^a	1017	9.83
C ₂ H ₅ OH	15:2	1.31	7.3 × 10 ⁻¹⁸	1044	9.58
CO	15:0.8	2.15	1.7 × 10 ⁻¹⁷ ^b	2137	4.68
			1.7 × 10 ⁻¹⁷	2152 Shoulder	4.65
CO ₂	15:0.8	1.37	2.1 × 10 ⁻¹⁶ ^b	2342	4.27
CH ₃ COH	15:0.7	1.37	6.1 × 10 ⁻¹⁸	1350	7.41
H ₂ CO	15:0.4	2.01	4 × 10 ⁻¹⁸ ^c	1496	6.68

^a Hudgins *et al.* (1993). Weak interstellar mixture.

^b Sandford *et al.* (1988).

^c Schutte *et al.* (1993).

irradiate the ice films. A nickel beam foil was used to separate the vacuum of the accelerator from the clean vacuum of the cryostat area. The measured energy of protons after passing through this foil was 0.8 MeV. The protons passed through the ice and came to rest in the aluminum substrate resulting in a current (typically 0.5–1 × 10⁻⁷ amps) which was measured to determine the radiation dose. The stopping power (eV cm² g⁻¹) for 0.8-MeV protons in each ice mixture was calculated from the weighted average of the stopping power for each molecular component. Stopping power multiplied by the beam fluence (protons cm⁻²) and divided by the average molecular density gave the dose (eV absorbed average-amu-molecule⁻¹). We converted each dose to eV (18 amu)⁻¹, which we call simply eV molecule⁻¹. A fluence of 1.5 × 10¹⁵ protons cm⁻² was near 17 eV molecule⁻¹. *G*-values (number of molecules altered per 100 eV absorbed energy), also called “yield,” were calculated by knowing the fraction of new product relative to the unirradiated ice ratio.

RESULTS

The results of four irradiation experiments are discussed in this paper: In Experiment 1, icy mixtures of H₂O + CH₄ with different concentrations were irradiated to determine the resulting yield of C₂H₆. In Experiment 2, the formation of C₂H₆ in irradiated H₂O + C₂H₂ mixtures was studied. In Experiment 3, both CH₄ and C₂H₂ in a water-dominated mixture were irradiated to form C₂H₆. Finally, in Experiment 4 the radiation products from a four-component ice mixture (H₂O + CH₄ + C₂H₂ + CO) were examined. In all experiments, C₂H₆ was synthesized, along with other organic molecules.

A. Experiment 1

Three ices with different H₂O : CH₄ concentrations, 2 : 1, 7 : 1, and 15 : 1, were irradiated in steps. IR spectra after each irradiation dose showed progressive changes in the strength of new features in the ice. Figure 1 is the spectrum of the mixture richest in CH₄ before and after irradiation to a dose of 33 eV molecule⁻¹. This rich mixture was chosen since its spectral features are most pronounced; all H₂O + CH₄ mixtures formed the same products although some of the least abundant species were not detected in the 15 : 1 mixture. The C₂H₆ feature identified on the wing of the H₂O band at 2976 cm⁻¹ after irradiation was used to determine the C₂H₆ column density as a function of dose. New species, other than CO₂ and CO, are most easily identified in the expanded spectrum from 2000 to 800 cm⁻¹ shown in Fig. 2. New features were identified by comparison with appropriate reference spectra which are shown stacked below the H₂O + CH₄ spectrum. The same techniques used to form the experimental ices were used when condensing these reference ices.

Figure 3 summarizes the column density of C₂H₆ formed in the three different H₂O + CH₄ ices as a function of proton dose. All experiments were normalized to a mixture whose CH₄ initial column density was 2.3 × 10¹⁸ CH₄ cm⁻². The column density of C₂H₆ reaches a plateau around 5–10 eV molecule⁻¹. Our data show the amount of C₂H₆ formed was directly related to the initial concentration of CH₄ in the mixture. Hudson and Moore (1997) discussed H-atom abstraction from CH₄, followed by the dimerization of the resulting CH₃ radical as a likely formation mechanism for C₂H₆. This mechanism is most efficient when the nearest

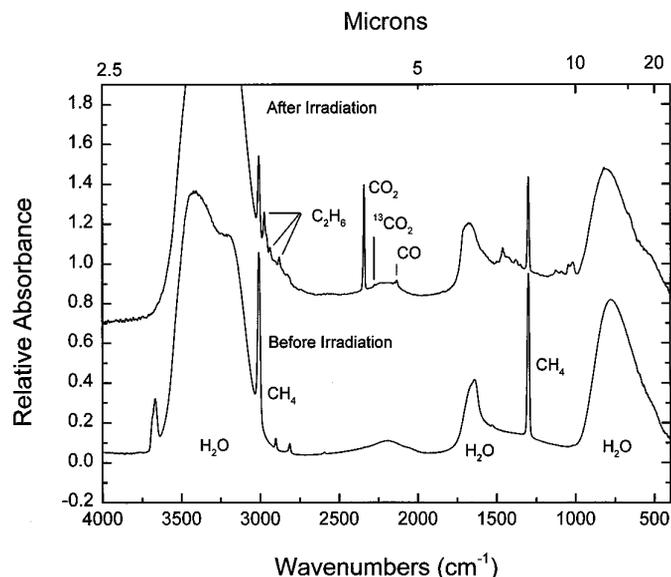


FIG. 1. Mid-infrared spectrum of an H₂O + CH₄ (2:1) ice at *T* < 20 K before and after proton irradiation to a dose of 33 eV molecule⁻¹.

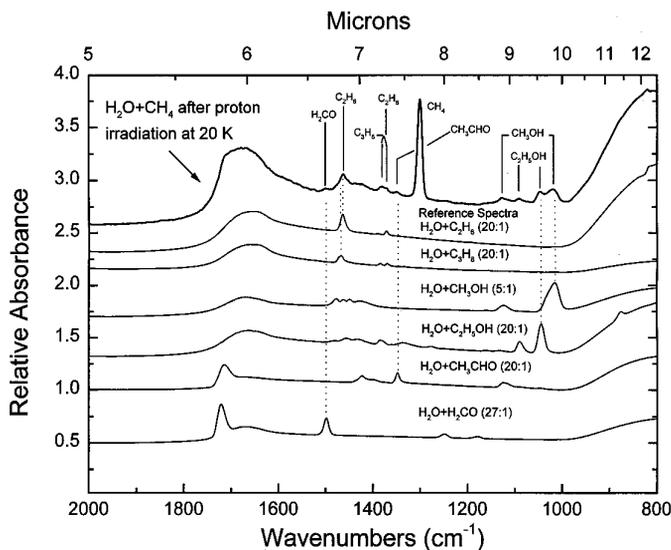


FIG. 2. Synthesized species in irradiated $\text{H}_2\text{O} + \text{CH}_4$ ice ($2000\text{--}800\text{ cm}^{-1}$) were identified by comparing the irradiated ice spectrum with ice reference spectra of dilute mixtures of organics with water at $T < 20\text{ K}$.

neighbor to a CH_3 radical is another CH_3 , and least efficient when CH_3 is surrounded by H and OH fragments, as is typical of the 15:1 and 7:1 mixtures.

To illustrate the changes in column density of product species with proton dose, data for the $\text{H}_2\text{O} + \text{CH}_4$ (7:1) mixture have been plotted in Fig. 4. As the dose increased, a plateau was reached in the formation of alcohols, but CO_2 , CH_3CHO , and H_2CO continued to slowly rise, whereas CO and C_3H_8 slowly decreased. Table II compares the column densities of each of these components for the three $\text{H}_2\text{O}:\text{CH}_4$ ice concentrations after a proton dose of $17\text{ eV molecule}^{-1}$ (a dose high enough to reach a plateau

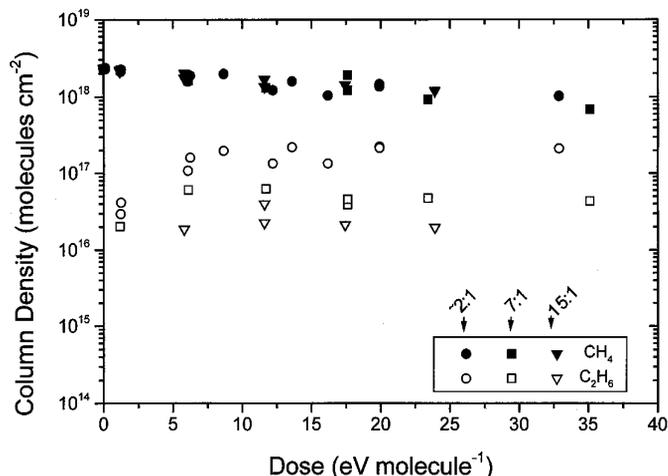


FIG. 3. Changes in CH_4 and C_2H_6 during proton irradiation of $\text{H}_2\text{O} + \text{CH}_4$ mixtures at $T < 20\text{ K}$.

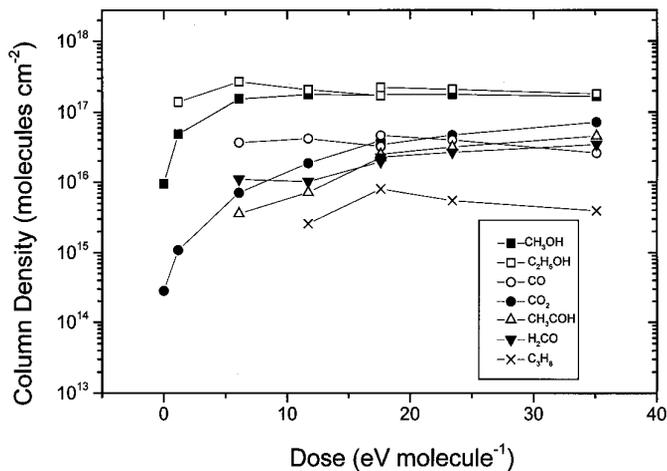


FIG. 4. Changes in column density of synthesized molecules other than C_2H_6 in $\text{H}_2\text{O} + \text{CH}_4$ (7:1) during proton irradiation at $T < 20\text{ K}$.

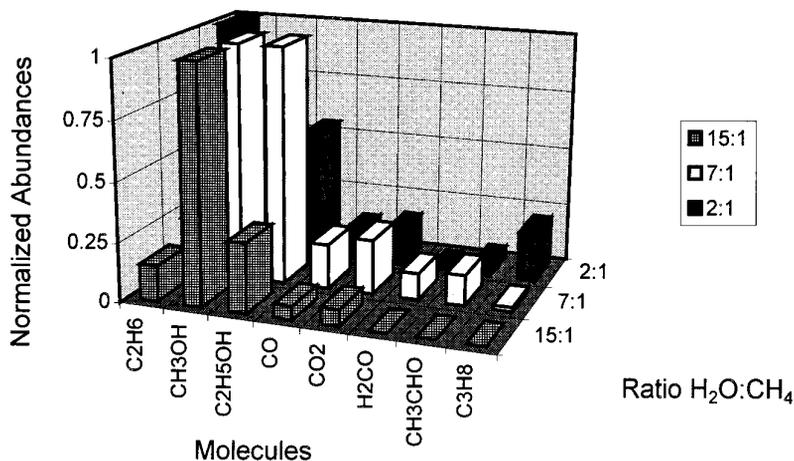
for those components which level out and one that is common to all experiments in this paper). A negative G -value for CH_4 indicates a decrease in column density; synthesized molecules have positive G -values. The bar graph in Table II summarizes the results; each experiment was normalized to the product with the largest column density in that particular experiment.

B. Experiment 2

Two different concentrations of $\text{H}_2\text{O} + \text{C}_2\text{H}_2$ were irradiated, 4:1 and 15:1. Figure 5 is the spectrum of $\text{H}_2\text{O}:\text{C}_2\text{H}_2$ (4:1) before and after proton irradiation to a dose of $17\text{ eV molecule}^{-1}$. Unlike irradiated pure acetylene, neither diacetylene nor polymers were detected when C_2H_2 was irradiated with H_2O . The identification of C_2H_6 as a radiation product and the calculation of its column density was done using the bands on the wing of the water feature at 2976 cm^{-1} . Many new features are identified in the expanded spectrum in the $2000\text{ to }800\text{ cm}^{-1}$ range shown in Fig. 6. Ethylene, C_2H_4 , was identified by comparison with a reference spectrum of $\text{H}_2\text{O} + \text{C}_2\text{H}_4$ (20:1). The column density of C_2H_2 continuously decreased during irradiation, C_2H_4 increased and then began to decrease, and C_2H_6 continuously increased. This observation is consistent with the idea that H atoms, produced by the proton irradiation of H_2O , react with C_2H_2 in a stepwise fashion, creating C_2H_4 , which then is used to form C_2H_6 (Hudson and Moore 1997). Experiments on irradiated $\text{H}_2\text{O} + \text{C}_2\text{H}_4$ (spectra not shown) showed the conversion of C_2H_4 into C_2H_6 followed by the rise in $\text{C}_2\text{H}_5\text{OH}$ and a lag in the increase in CH_3OH to a value about an order of magnitude less than the $\text{C}_2\text{H}_5\text{OH}$ after $17\text{ eV molecule}^{-1}$. Irradiated $\text{H}_2\text{O} + \text{C}_2\text{H}_6$ (spectra not shown) showed that the fate of C_2H_6 was mainly the formation of $\text{C}_2\text{H}_5\text{OH}$ with an abundance

TABLE II
Comparison of Molecules Synthesized after 17 eV Molecule⁻¹ in H₂O + CH₄ Ices with Different Initial Concentrations

New species identified	Mixture 2:1	Column Density	<i>G</i>	Mixture 7:1	Column density	<i>G</i>	Mixture 15:1	Column density	<i>G</i>
	H ₂ O [2] CH ₄ [1] ΔCH ₄	2.3 × 10 ¹⁸ 9.0 × 10 ¹⁷	-1.34	H ₂ O [7] CH ₄ [1] ΔCH ₄	2.3 × 10 ¹⁸ 1.2 × 10 ¹⁸	-0.38	H ₂ O [15] CH ₄ [1] ΔCH ₄	2.3 × 10 ¹⁸ 8.7 × 10 ¹⁷	-0.23
C ₂ H ₆		2.2 × 10 ¹⁷	0.22		3.9 × 10 ¹⁶	0.01		2.1 × 10 ¹⁶	0.004
C ₂ H ₄									
CH ₃ OH		1.3 × 10 ¹⁷	0.13		1.7 × 10 ¹⁷	0.06		1.4 × 10 ¹⁷	0.02
C ₂ H ₅ OH		1.2 × 10 ¹⁷	0.12		1.7 × 10 ¹⁷	0.06		4.1 × 10 ¹⁶	0.007
CO		2.8 × 10 ¹⁶	0.03		3.2 × 10 ¹⁶	0.01		8.0 × 10 ¹⁵	0.001
CO ₂		3.4 × 10 ¹⁶	0.03		3.9 × 10 ¹⁶	0.01		9.8 × 10 ⁵	0.002
H ₂ CO					1.9 × 10 ¹⁶	0.006			
CH ₃ CHO		1.1 × 10 ¹⁶	0.01		2.2 × 10 ¹⁶	0.008			
CH ₄									
C ₃ H ₈		4.5 × 10 ¹⁶	0.04		3.0 × 10 ¹⁵	0.001			



an order of magnitude more than CH₃OH after 17 eV molecule⁻¹.

C. Experiments 3 and 4

The IR spectra of H₂O + CH₄ + C₂H₂ (15:0.6:1) before and after irradiation to a dose of 17 eV molecule⁻¹ is shown in Fig. 7. In this experiment an expansion of the region between 2000 and 800 cm⁻¹ is not shown because it revealed the same array of products as identified in Experiment 2 along with the sequence C₂H₂ → C₂H₄ → C₂H₆. Experiment 4 involved a four-component mixture, namely H₂O + CH₄ + C₂H₂ + CO (10:0.8:1:0.2). This experiment (spectra not shown) showed more CO₂ and H₂CO formation than Experiment 3, due to the initial presence of CO, but otherwise produced the same array of products. Table III summarizes the column density of new molecules synthesized after proton irradiation in all four experiments and lists the calculated *G* value for each product. In this

table the more dilute mixtures are compared. Table IV summarizes the peak positions of molecules synthesized in all four experiments. Here the richer mixtures were used, when available, because they gave the most intense signatures for new molecules.

DISCUSSION

Our determination of C₂H₆ yields in different water + hydrocarbon mixtures, and the identification of new infrared features, constitutes a more detailed study of the radiation products than previously available. These experiments show how the radiation products in an H₂O ice differ from those in a pure hydrocarbon, and are dependent on the initial H₂O abundance. Specifically, the results summarized in Table II for H₂O + CH₄ ice irradiations show increased C₂H₆ formation with increasing initial CH₄ abundance (decreasing H₂O abundance). Further, in our H₂O:CH₄ = 2:1 strongest mixture, the C₂H₆ yield is higher than that

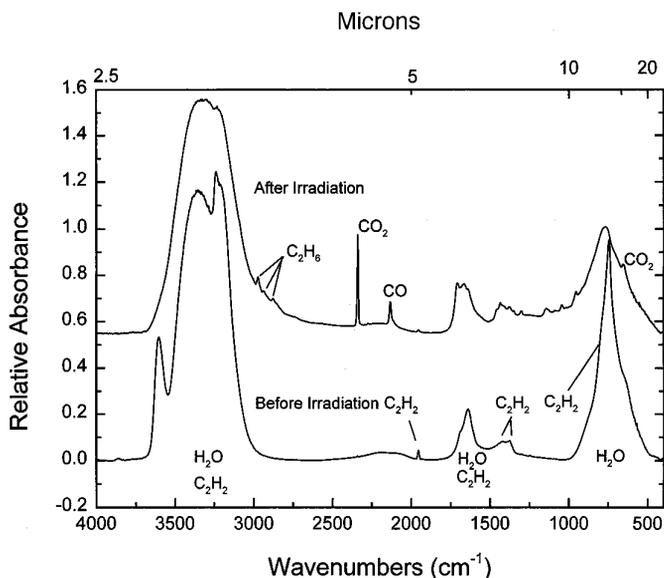


FIG. 5. Mid-infrared spectrum of an $\text{H}_2\text{O} + \text{C}_2\text{H}_2$ (4:1) ice at $T < 20$ K before and after irradiation to a dose of $17 \text{ eV molecule}^{-1}$.

of any other product. In contrast, with the weaker $\text{H}_2\text{O} + \text{CH}_4$ mixtures CH_3OH has higher yields than C_2H_6 .

The dependence of the C_2H_6 and CH_3OH yields on the initial $\text{H}_2\text{O} : \text{CH}_4$ ratio can be understood in terms of well-known radiation chemical reactions. Proton irradiation of CH_4 initiates a set of rapid reactions with the end result being the formation of H atoms and methyl (CH_3) radicals:

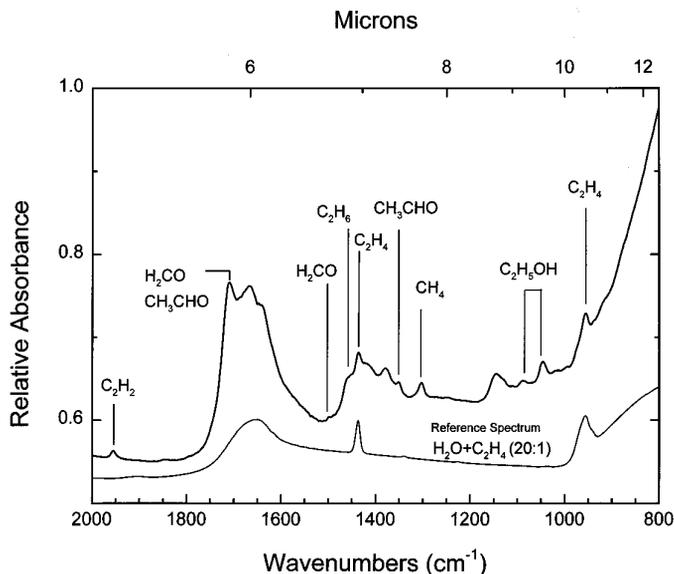


FIG. 6. Synthesis of C_2H_4 in irradiated $\text{H}_2\text{O} + \text{C}_2\text{H}_2$ ice ($2000\text{--}800 \text{ cm}^{-1}$) was confirmed by comparing the irradiated ice spectrum with $\text{H}_2\text{O} + \text{C}_2\text{H}_4$ (20:1). New species other than C_2H_4 were identified using reference spectra shown in Fig. 2.

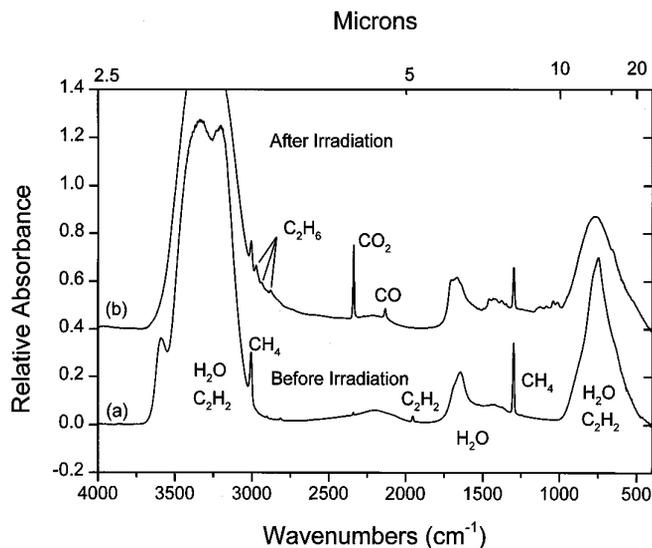


FIG. 7. Infrared spectrum of an $\text{H}_2\text{O} + \text{CH}_4 + \text{C}_2\text{H}_2$ (15:0.6:1) ice at $T < 20$ K before and after irradiation to a dose of $17 \text{ eV molecule}^{-1}$.



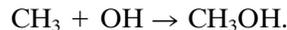
The reactive methyl radicals subsequently dimerize to form C_2H_6 :



However, when H_2O is present proton irradiation also produces H atoms and hydroxyl (OH) radicals:



So in cases in which both CH_4 and H_2O are initially present the CH_3 from CH_4 can react with OH from H_2O to form CH_3OH , in competition with CH_3 dimerization to produce C_2H_6 :



This means that C_2H_6 production should be greatest when the H_2O concentration is smallest, as was observed. In the presence of H_2O this last reaction ensures CH_3OH production.

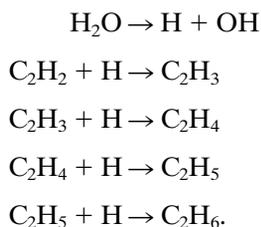
Table V summarizes the $\text{C}_2\text{H}_6 : \text{CH}_4$ ratios in our irradiated $\text{H}_2\text{O} + \text{CH}_4$ mixtures (Experiment 1). Despite the ready production of C_2H_6 , Table V shows that none of the three $\text{C}_2\text{H}_6 : \text{CH}_4$ ratios is as large as those observed in Hyakutake or Hale-Bopp. Irradiation of simple, binary $\text{H}_2\text{O} + \text{CH}_4$ mixtures failed to convert enough CH_4 to C_2H_6 . In contrast, our $\text{H}_2\text{O} + \text{C}_2\text{H}_2$ ices (Experiment 2) produced yields of C_2H_6 of the same order of magnitude as in $\text{H}_2\text{O} + \text{CH}_4$ ices (Table III) but the ratios generally

TABLE III
Summary of New Molecules Synthesized after Proton Irradiation (17 eV molecule⁻¹)

New species identified	Experiment 1		Experiment 2		Experiment 3		Experiment 4	
	Column density	<i>G</i>	Column density	<i>G</i>	Column density	<i>G</i>	Column density	<i>G</i>
H ₂ O [15]			H ₂ O [15]		H ₂ O [15]		H ₂ O [10]	
CH ₄ [1]	2.3 × 10 ¹⁸		C ₂ H ₂ [1]	1.67 × 10 ¹⁸	CH ₄ [0.6]	6.0 × 10 ¹⁷	CH ₄ [0.8]	6.14 × 10 ¹⁷
Δ CH ₄	8.7 × 10 ¹⁷	-0.23	Δ C ₂ H ₂	1.61 × 10 ¹⁸	C ₂ H ₂ [1]	1.02 × 10 ¹⁸	C ₂ H ₂ [1]	7.36 × 10 ¹⁷
					Δ CH ₄	2.1 × 10 ¹⁷	CO [0.2]	1.62 × 10 ¹⁷
					Δ C ₂ H ₂	9.4 × 10 ¹⁷	Δ CH ₄	2.6 × 10 ¹⁷
							Δ C ₂ H ₂	6.6 × 10 ¹⁷
							Δ CO	7.3 × 10 ¹⁶
								-0.21
								-0.52
								-0.06
C ₂ H ₆	2.1 × 10 ¹⁶	0.004	4.4 × 10 ¹⁶	0.008	6.2 × 10 ¹⁶	0.02	4.9 × 10 ¹⁶	0.04
C ₂ H ₄			2.1 × 10 ¹⁶	0.004	1.9 × 10 ¹⁶	0.007		
CH ₃ OH	1.4 × 10 ¹⁷	0.02	5.0 × 10 ¹⁶	0.009	3.4 × 10 ¹⁶	0.01	5.0 × 10 ¹⁶	0.04
C ₂ H ₅ OH	4.1 × 10 ¹⁶	0.007	1.1 × 10 ¹⁷	0.02	1.2 × 10 ¹⁷	0.04	3.8 × 10 ¹⁶	0.03
CO	8.0 × 10 ¹⁵	0.001	9.1 × 10 ¹⁶	0.017	4.5 × 10 ¹⁶	0.002		
CO ₂	9.8 × 10 ¹⁵	0.002	4.6 × 10 ¹⁶	0.009	1.4 × 10 ¹⁶	0.005	3.2 × 10 ¹⁶	0.03
H ₂ CO			6.8 × 10 ¹⁵	0.001	4.5 × 10 ¹⁵	0.002	7.4 × 10 ¹⁵	0.006
CH ₃ CHO			2.8 × 10 ¹⁶	0.005	1.3 × 10 ¹⁶	0.005	1.3 × 10 ¹⁶	0.01
CH ₄			5.6 × 10 ¹⁶	0.01				
C ₂ H ₈					1.1 × 10 ¹⁶	0.004	8.4 × 10 ¹⁵	0.007

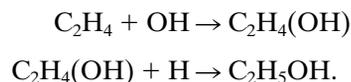
compared better with cometary values. Table V gives C₂H₆:CH₄ and C₂H₆:C₂H₂ ratios for our H₂O + C₂H₂ experiments and also for Hyakutake and Hale-Bopp. The C₂H₆:CH₄ and C₂H₆:C₂H₂ ratios from our 15:1 experiment compare favorably to both of the Hyakutake ratios. However, for Comet Hale-Bopp, the same comparison shows that our C₂H₆:CH₄ ratio matches the Hale-Bopp value but our C₂H₆:C₂H₂ ratio is much too small.

To explain the production of cometary C₂H₆, Mumma *et al.* (1996) suggested hydrogen-atom additional reactions. This proposal certainly is consistent with all results from our Experiment 2. H atoms arise from proton irradiation of H₂O, and then add sequentially to C₂H₂ to form C₂H₄ and then C₂H₆. These reactions have been described previously (Hudson and Moore 1997):

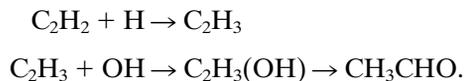


There is little chance of detecting the intermediate C₂H₃ (vinyl) and C₂H₅ (ethyl) radicals with our IR methods, which are not particularly sensitive to low concentrations of reactive intermediates. However, some additional evidence for this pathway to C₂H₆ comes from the fact that H atom reactions take place in competition with OH radical

addition reactions. This means that H and OH addition to C₂H₄ should result in C₂H₅OH formation, which is observed:



It is possible, of course, for hydroxyl radicals to add directly to the original C₂H₂ molecules. However, the addition of OH and H to acetylene usually results in a rearrangement to the more stable product, acetaldehyde (CH₃CHO):



Acetaldehyde was indeed an observed product in our H₂O + C₂H₂ experiments.

We have not investigated the mechanism for synthesis of CH₄ in our H₂O + C₂H₂ mixtures (Experiment 2). One possibility is the initial formation of C₂H₆ from C₂H₂, followed by dissociation into CH₃ radicals. Subsequent H-atom addition, or H-atom abstraction from another molecule, would convert CH₃ into CH₄. Alternatively, one or more excited states of C₂H₂ may lead to dissociation into CH radicals which quickly form CH₄, or perhaps insertion reactions are relevant (Roessler 1992). For the present, such possibilities remain speculative.

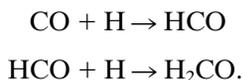
The most complex mixtures we irradiated were in our Experiments 3 and 4, and Table V gives the C₂H₆:CH₄ and C₂H₆:C₂H₂ ratios measured in those experiments.

TABLE IV
Identification of Synthesized Molecules and Their Band Positions (cm⁻¹)

New species identified	Experiment 1	Experiment 2	Experiment 3	Experiment 4
	H ₂ O [2] CH ₄ [1]	H ₂ O [4] C ₂ H ₂ [1]	H ₂ O [10] CH ₄ [0.6] C ₂ H ₂ [1]	H ₂ O [10] CH ₄ [0.8] C ₂ H ₂ [1] CO [0.2]
C ₂ H ₆	2975 2940 2881 1464 1373 wmix 821	2975 2939 2880 1461 sh	2975 2939 2880 1461 816 w 1436	2975 2941 2882 1463
C ₂ H ₄		1436 955	1436	820 w
CH ₃ OH	1128 1020		1127 1016	1130 1018
C ₂ H ₅ OH	1091 1047	1090 1046	1088 1046	1089 1046
CO	2136 2152	2134	2135	2136
CO ₂	2342	2340 649	2341 649	2341 650
¹³ CO ₂	2275	2274	2275	2276
H ₂ CO	1500	1499	1499	1499
CH ₃ CHO	1351	1351	1351	1351
CH ₄		1303		
C ₃ H ₈	2962 sh 1373 wmix 1463 w 1384 w		2960 sh	2960 sh

Note. w, weak; sh, shoulder; wmix, weak and mixed with peaks from other molecules.

Both ratios are smaller in Experiment 4, which included CO in the initial mixture, than in Experiment 3, which did not. CO competes with C₂H₂ for atoms in Experiment 4, reducing the formation of C₂H₆. Hydrogen-atom addition reactions to CO can be written which lead to HCO (formyl radical) and H₂CO (formaldehyde), and both were observed in our experiments:



In both Experiments 3 and 4 the C₂H₆:C₂H₂ ratio compares well with that found in Hyakutake but is lower than in Hale–Bopp. The C₂H₆:CH₄ ratios in Experiments 3 and 4 are too low compared to that seen in both comets. Comparing the C₂H₆:CH₄ ratios from Experiment 3 (H₂O + C₂H₂ + CH₄) and Experiment 2 (H₂O + C₂H₂ only) suggests that it is the initial presence of CH₄ which drops our laboratory ratios to unrealistic values. In addition, we found no evidence that CH₄ ever forms C₂H₂ in any experiments; no C₂H₂ production was observed in H₂O + CH₄ experiments. (In fact, C₂H₂ production was not found in any of our irradiated ices.) All of these obser-

vations argue against a strong role for CH₄ in the radiation chemistry of cometary ice analogs relevant to comets like Hyakutake and Hale–Bopp and suggest that C₂H₂ is part of the natal cometary ice prior to processing. As a source of C₂H₆, CH₄ is equally as efficient as C₂H₂ but CH₄ cannot be used to explain the large abundance of C₂H₂ in the ice.

Although the focus of this paper is hydrocarbons, a few other molecules should be mentioned. Two important cometary molecules are CO and CO₂ and both of these were observed in our experiments, with abundances given in Table V. Experiments beginning with H₂O + CH₄ mixtures gave a CO:CO₂ ratio of 0.8 in all cases, but experiments with H₂O + C₂H₂ mixtures gave CO:CO₂ = 6.4 and 2.0 for the 4:1 and 15:1 mixtures, respectively. Our Experiments 3 and 4 gave CO:CO₂ ratios of 3 and 2.8, respectively. For comparison, observations of Hale–Bopp by Crovisier *et al.* (1997) gave CO:CO₂ ≈ 3 at ~3 AU. CO abundances of ~10% (Weaver *et al.* 1998) and ~20% (Crovisier 1998) relative to H₂O have been reported. For Hyakutake, observations by Weaver *et al.* (1996) gave CO:CO₂ ≈ 1, with a CO abundance of ~6%, again relative to H₂O (Weaver *et al.* 1996, Mumma *et al.* 1996). See also the discussion of CO and CO₂ variations by Bockelée-Morvan (1997).

Finally, we address the formation of alcohols in our experiments. Methanol (CH₃OH) is an abundant component of interstellar ice, ~10% relative to H₂O (Grim *et al.* 1991, Allamandola *et al.* 1992, Schutte *et al.* 1996), although the abundance varies with the source to as high as 50%. In cometary comae the CH₃OH abundance is also variable with higher values being around 5% (Mumma 1997). The reported abundance of CH₃OH in Hyakutake varies from 0.5 to 2%, relative to H₂O (Womack *et al.* 1996, Womack *et al.* 1997, Matthews *et al.* 1996), and in Hale–Bopp is roughly 2% (Biver *et al.* 1997). There has been no identification of ethanol (C₂H₅OH) either in cometary comae or in interstellar ices. Ethanol has been detected in the gas phase in star-forming regions with abundances similar to those of methanol in hot molecular cores associated with regions of massive star formation.

Thus it is relevant that both CH₃OH and C₂H₅OH were identified as radiation products in our Experiments 1–4. Table III shows that the CH₃OH yield in our experiments was about twice that of C₂H₅OH in mixtures initially containing H₂O and CH₄ but that the reverse was true in mixtures initially containing H₂O and C₂H₂. In other words the single-carbon alcohol dominated in mixtures with CH₄ (Experiment 1) and the two-carbon alcohol dominated in mixtures with C₂H₂ (Experiment 2), as expected. Moreover, the radiation yields (*G* values) of the alcohols were comparable to and usually higher than the yields of C₂H₆ in all experiments. Furthermore, H and OH addition reactions are sufficiently efficient to explain both the formation of C₂H₆ as well as the alcohols.

TABLE V
Ratios of Synthesized Products Compared to Volatile Species Observed in Comets

	C ₂ H ₆ :CH ₄	C ₂ H ₆ :C ₂ H ₂	Approximate observed volatile ratios H ₂ O:CO:CH ₄ :C ₂ H ₆ :C ₂ H ₂ :CH ₃ OH
Comet Hyakutake	0.6–1.7	0.4–4	100:6:0.7:0.4–1.2:0.3–0.9:0.5–2
Comet Hale–Bopp	0.77	5.3	100:10–20:0.62:0.48:0.09:2
			Approximate laboratory ice ratios after 17 eV molecule ⁻¹ irradiation H ₂ O:CO:CH ₄ :C ₂ H ₆ :C ₂ H ₂ :CH ₃ OH
Experiment 1 H ₂ O + CH ₄			
2:1	0.17	No C ₂ H ₂	100:0.6:30:5:0:3
7:1	0.03	No C ₂ H ₂	100:0.2:7:0.2:0:1
15:1	0.02	No C ₂ H ₂	100:0.2:4:0.06:0:0.4
Experiment 2 H ₂ O + C ₂ H ₂			
4:1	1.9	0.2	100:2:0.6:1.2:6:0.02
15:1	0.8	0.8	100:0.4:0.2:0.2:0.2:0.2
Experiment 3 H ₂ O + CH ₄ + C ₂ H ₂			
15:0.6:1	0.2	1	100:0.3:2:0.4:0.5:0.2
Experiment 4 H ₂ O + CH ₄ + C ₂ H ₂ + CO			
10:0.8:1:0.2	0.14	0.6	100:2:5:0.7:1:0.7

In conclusion, our experiments demonstrate that both dimerization and H-atom addition reactions in irradiated water-rich 15 K ices containing CH₄ or C₂H₂, respectively, can produce sufficient yields of C₂H₆ to explain the cometary observation of C₂H₆. No evidence was found for C₂H₂ formation in any of our experiments, which suggests that C₂H₂ is part of the natal ice composition. These results support the proposal by Mumma *et al.* (1996) that solid-phase reactions could produce the chemical ratios observed in Hyakutake. CO and CO₂ were always detected as radiation products; other products were CH₃OH, C₂H₅OH, H₂CO, C₃H₈, and CH₃COH. The synthesis of CH₃OH and C₂H₅OH supports an idea discussed by Charnley *et al.* (1995) that grain-surface chemistry may well contribute to alcohol synthesis in interstellar ices, as opposed to gas-phase chemistry alone.

ACKNOWLEDGMENTS

M. Mumma is acknowledged for discussions on molecules detected in Comet Hyakutake and Comet Hale–Bopp. Discussions with Neil Dello Russo also are acknowledged. Theresa Smith is thanked for experimental assistance. R.L.H. thanks the NASA/ASEE Summer Faculty Fellowship program for support (summer, 1996 and 1997) and acknowledges earlier assistance under NASA Grant NAG 5-1843. Both authors acknowledge NASA funding through RTOP 344-33-01 and 344-02-57.

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